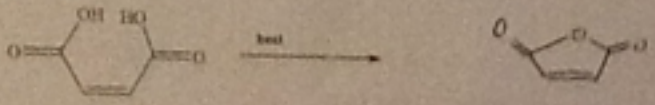
Value [34]

PART A

1. This question has 17 parts. Answer **ALL** parts.

For each of the following reactions, provide structures for all the organic products that are formed. Indicate the stereochemistry where appropriate. If more than one product is formed indicate major and minor products where applicable. If no reaction occurs write "No Reaction"

1)



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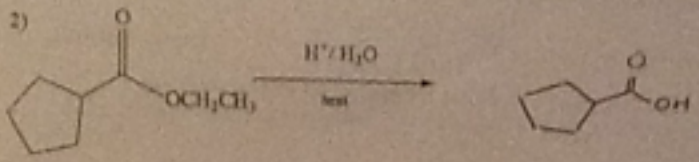

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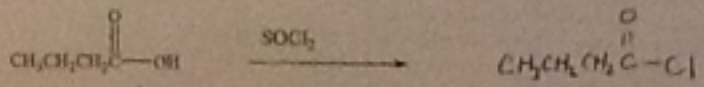

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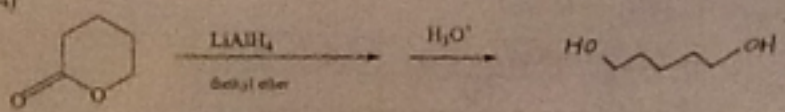

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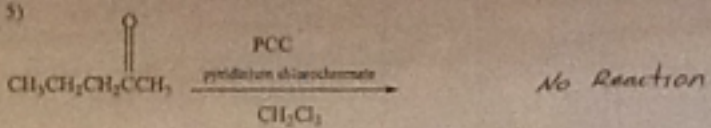

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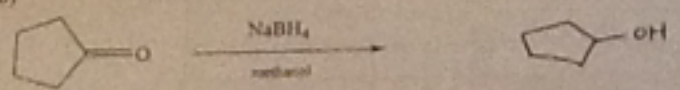

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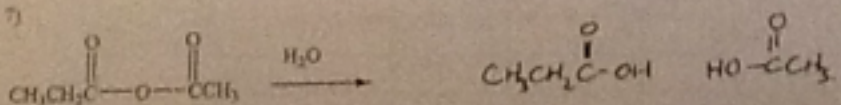

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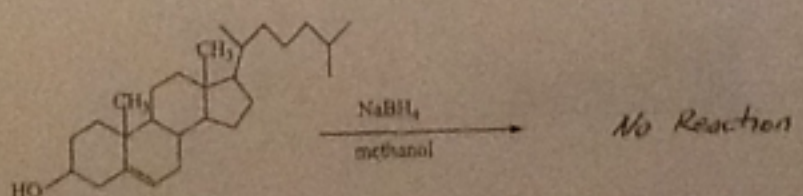

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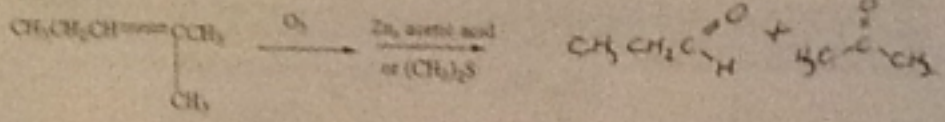

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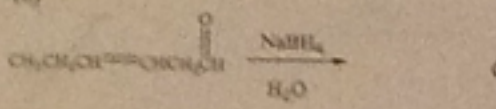

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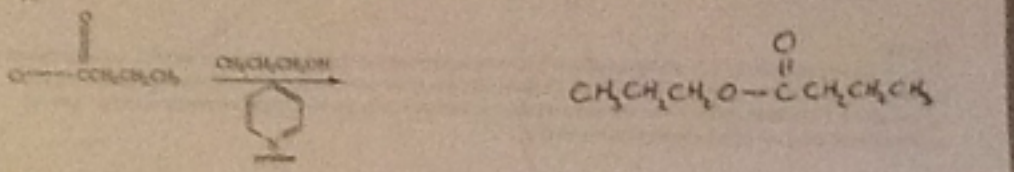

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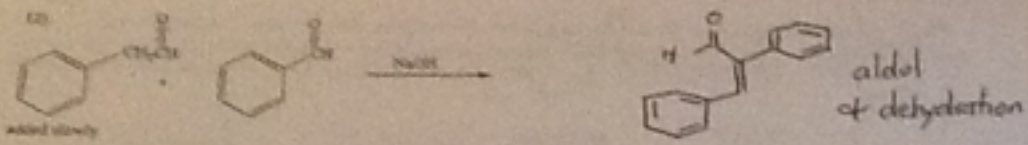

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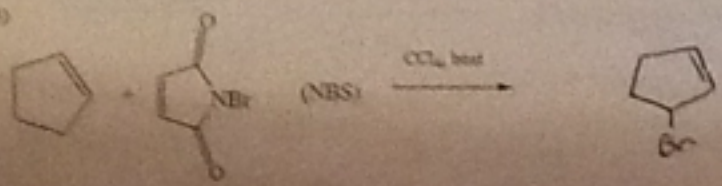

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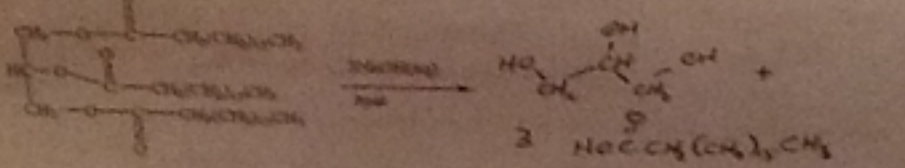

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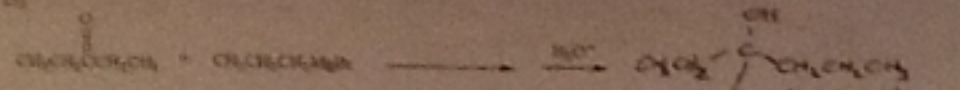

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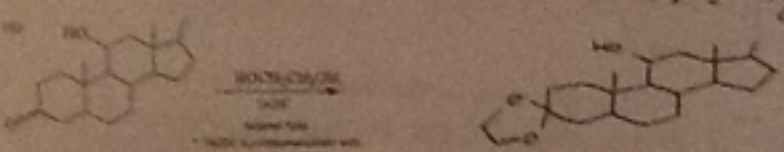

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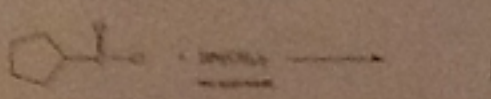
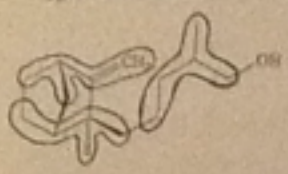


PART B

[Value]

[3] 2. The structure of a terpene or terpenoid is shown below (β-Santalol comes from sandalwood.). Classify it as a mono-, sesqui-, di-, sester- or triterpene etc, and clearly identify the isoprene units. Do not include oxygen atoms in the isoprene units.

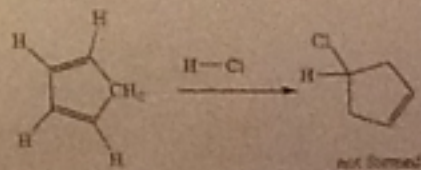
$C_{15}H_{26}O$ – sesquiterpene



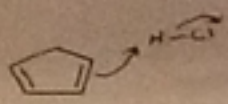
beta santalol

[Value]

[?] 3. In the reaction of 1,3-cyclopentadiene with one equivalent of hydrogen chloride at 0°C, no significant amount of 4-chlorocyclopentene is produced. Explain this result by means of a detailed mechanism using the curved arrow formalism. Show what the main product is and how it is formed, and comment on why there is only one main product (ignoring stereochemistry.)



not formed



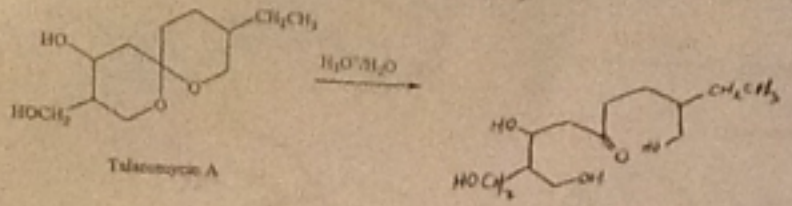
Protonation occurs to give the more stable allylic cation, rather than a secondary cation (NOT FORMED!)

Resonance gives the identical structure

$Cl^{\ominus}$

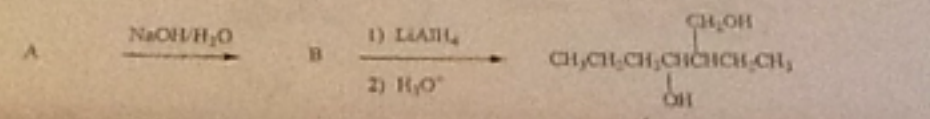
Only one intermediate cation is formed so only one product.

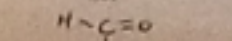
[Value]
[8] 4. Talaromycin A is a toxic substance produced by a fungus that grows on the "litter" in a poultry house. Treating talaromycin A with dilute aqueous acid at room temperature leads to the formation of a product which shows a strong absorption in the infrared near 1715 cm^{-1}. Propose (draw) a structure for this product, but don't concern yourself with stereochemistry.



Talaromycin A

[Value]
[8] 5. The compound 2-ethyl-1,3-hexanediol is the active ingredient in the insect repellant "6-12". This compound can be made by a short two step reaction sequence involving an aldol addition. Write the structural formulas for the reactant(s) A and the intermediate product B in the following sequence.





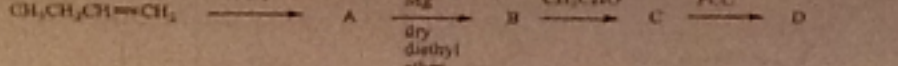
A = $CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}H$

Butanal

B = $CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}CHCH_2CH_3$

No dehydration in aldol reaction

[Value]
[8] 6. Give structural formulas for all the compounds A, B, C and D in the following synthetic sequence.



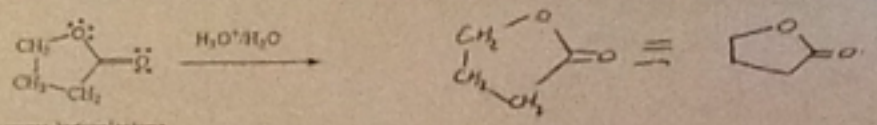
A = $CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3$

B = $CH_3CH_2\underset{\underset{MgBr}{|}}{CH}CH_3$

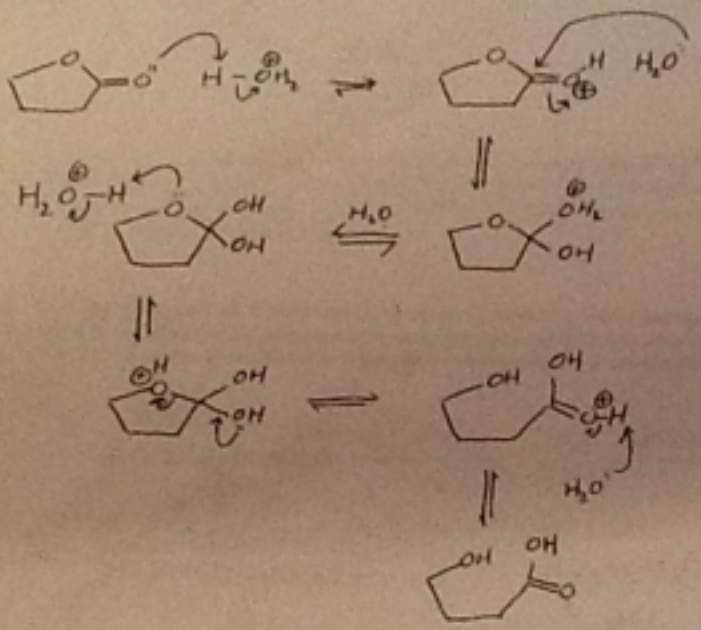
C = $CH_3CH_2\underset{\underset{HO-CHCH_3}{|}}{CH}CH_3$

D = $CH_3CH_2\underset{\underset{O=C-CH_3}{|}}{CH}CH_3$

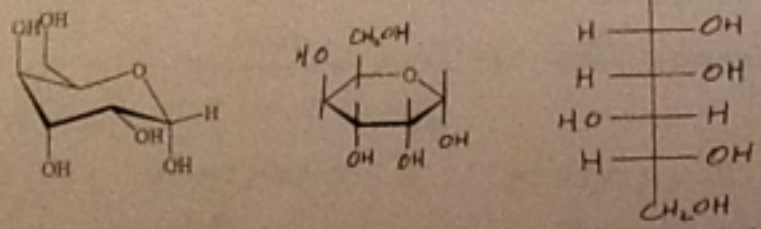
[Value]
[8] 7. γ-Butyrolactone (structure below) is a common ingredient in solvents used in paint removal. Its hydrolysis in aqueous acid is a normal ester hydrolysis. Using the curved arrow formalism, give a detailed mechanism for this hydrolysis.



gamma-butyrolactone



[Value]
[9] 8. (a) [5] The structure of gulose is shown. Redraw gulose, first as a Haworth projection of this anomer, and then as a Fischer projection of the open chain form, both using the templates provided.



(b) [4] Classify the gulose molecule given above by circling the appropriate response in each of the four pairs below.

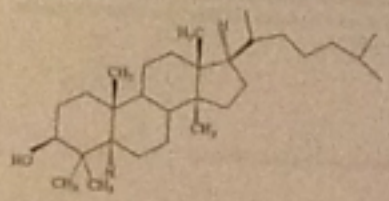
D or L

reducing or non-reducing

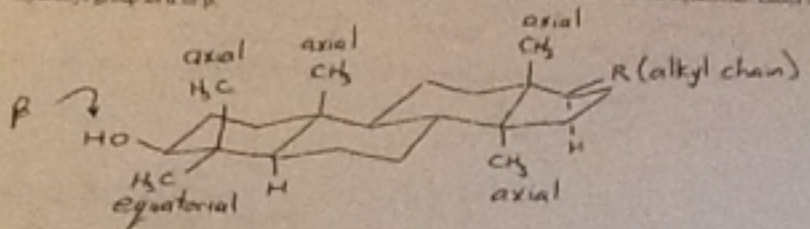
α or β

furanose or pyranose

[Value]
[9] 9. The following molecule is a hydrogenated form of lanosterol, one of the key intermediates in the biosynthesis of all steroid hormones.

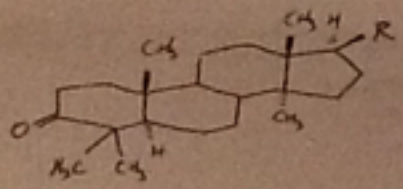


(a) [5] Draw a correct chair conformational representation of this steroid. Draw each substituent in its correct position and orientation, and label each ring methyl group as either axial or equatorial. Label the hydroxyl group as α or β.

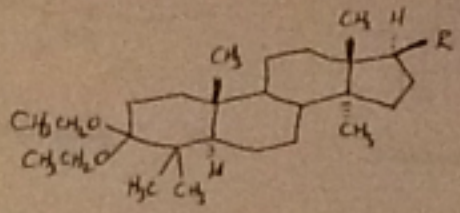


(b) [4] Show the product that would be obtained from the reaction of this steroid with each of the following reagents sequentially. (That is, the second set of reagents acts on the product from the first.) It is not necessary to use chair conformational drawings for this part.

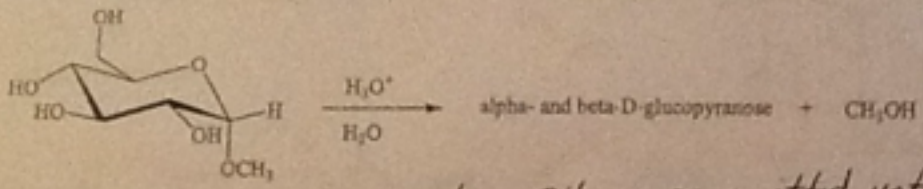
(i) pyridinium chlorochromate



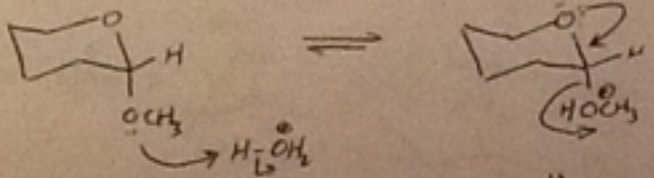
(ii) Excess CH_3CH_2OH and dilute acid

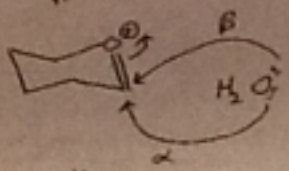


[Value]
[8] 10. a) Methyl glucopyranosides do not undergo mutarotation, nor do they show any of the aldehyde reactions that glucose exhibits. However, they are easily hydrolysed in acidic solution to give the equilibrium mixture of α-D-glucopyranose and β-D-glucopyranose. Using the curved arrow formalism, write a detailed mechanism that accounts for this hydrolysis. Show structures for all intermediates. Be sure to account for all products. (You may carefully abbreviate any non-reacting parts of the structures, but show the important details of any intermediates involved.)



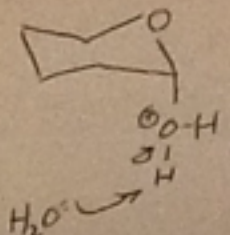
Non-reacting OH groups omitted until final product

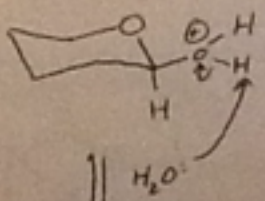


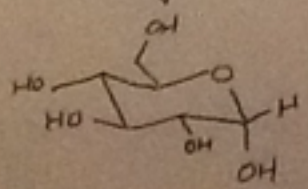


α - attack from bottom

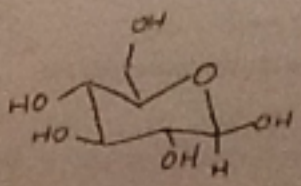
β - attack from top







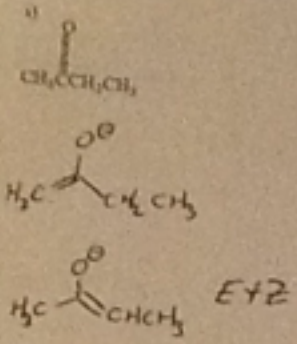
α-D-glucopyranoside



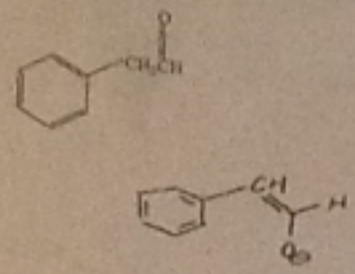
β-D-glucopyranoside

(value)
(12) 11. a) [6] Draw all of the enolate ions that can be formed from the following aldehydes or ketones.

i)

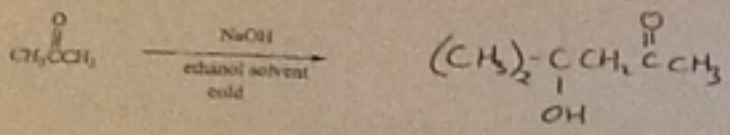


ii)

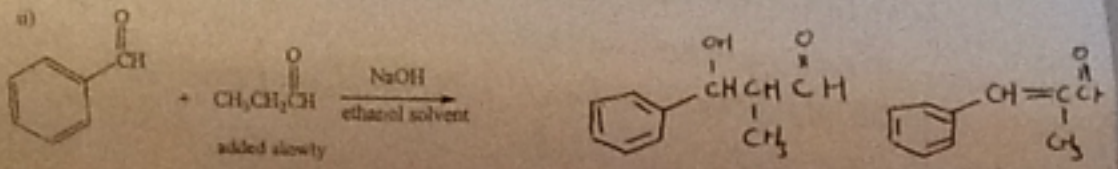


b) [4] Write structure(s) for the likely product(s) of the following aldol reactions.

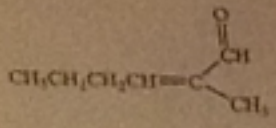
i)

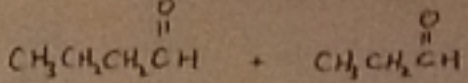


ii)

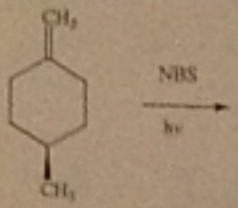


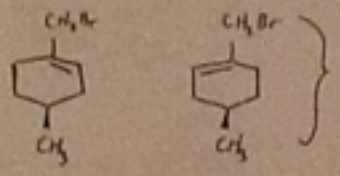
c) [2] Show the structure(s) of the starting material(s) that would be used to synthesize the following compound by an aldol condensation.



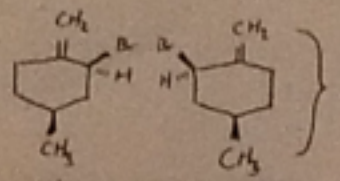


[Value]
[10] 12. The following allylic bromination (a radical reaction) results in six products, including stereoisomers. (NBS is N-bromosuccinimide.) Draw stereochemical structures for all six products. Does the product mixture contain any pairs of enantiomers? Oh yeah!

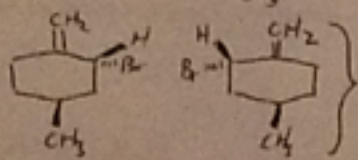




enantiomers

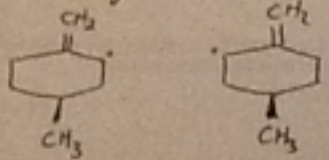


enantiomers



enantiomers

Explanation (not required to answer question):
Keeping the methyl group up (on the wedge bond), the radical intermediate can form on the "left" or "right" side:



These radicals are enantiomers

$Br\cdot$ attacks the CH_2 + forms a double bond in the ring ⇒ first two products.

$Br\cdot$ attacks the radicals shown from the same side as the CH_3 group ⇒ second two products

$Br\cdot$ attacks the radicals shown from the opposite side of the CH_3 ⇒ third two products